Uncertain Henry's Law Constants Compromise Equilibrium Partitioning Calculations of Atmospheric Oxidation Products

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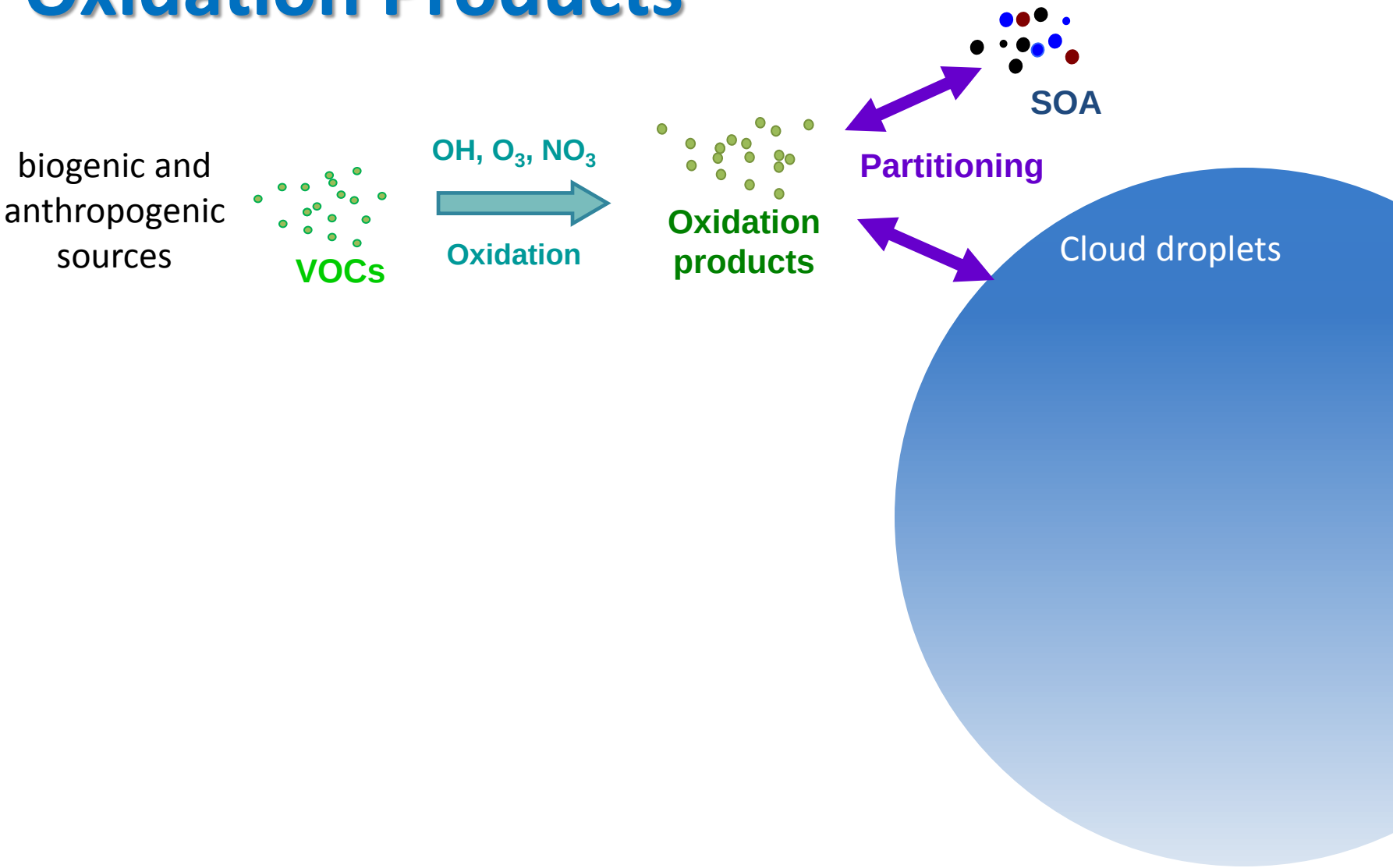
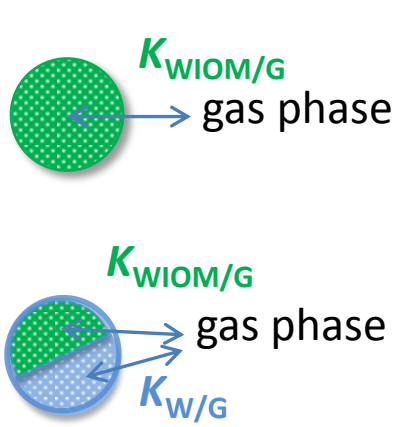
3 TEXAS A&M UNIVERSITY

Partitioning of Atmospheric Oxidation Products

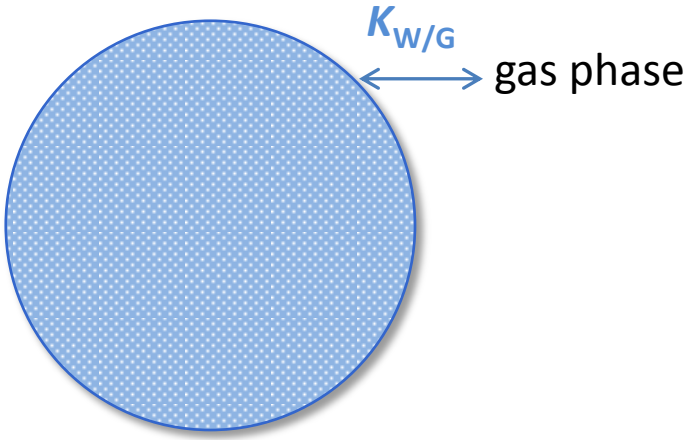


Atmospheric Phase Partitioning Equilibria

Aerosols (phase-separated or not)



Fog and cloud droplets



Organic phase (water insoluble organic matter, WIOM)

Aqueous phase (water, W)

Equilibrium partitioning coefficients

$K_{WIOM/G}$ between WIOM and gas phase.

$K_{W/G}$ between water and gas phase, i.e. Henry's law constant.

Atmospheric Oxidation Products

- large in number
- often with multiple functional groups
- high affinity for organic/aqueous phase

  (i.e. $K_{W/G}$ and $K_{WIOM/G}$ are large)
- experimental data not available

  → prediction required

Research Questions

- How well do partitioning prediction methods perform for atmospheric oxidation products?
- What determines the uncertainty of the phase partitioning prediction?
- Does the uncertainty in the prediction affect the estimated phase distribution of atmospheric oxidation products?

Three Prediction Methods

1. **ppLFERs**: polyparameter linear free energy relationships

$$\log K = c + aA + bB + sS + vV + lL$$

System parameters calibrated with experimental data for aerosol-gas and water-gas partitioning

+

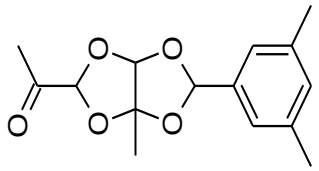
Solute descriptors describing intermolecular interactions (H-bond, polarity, cavity…) predicted with ABSOLV (ACD labs)

→ $K_{WIOM/G}$, $K_{W/G}$

2. **SPARC** Performs Automated Reasoning in Chemistry (on-line calculator)

SMILES (structures) of the organic compounds and "solvent" (WIOM or water)

→ $K_{WIOM/G}$, $K_{W/G}$



Structure of WIOM

3. **COSMOtherm**: COnductor like Screening MOdel for Realistic Solvents (COSMO-RS)

3D structures of the organic compounds and "solvent" (WIOM or water)

→ **Optimized 3D conformations** of the organic compounds and "solvent" (WIOM or water) with COSMOconf and Turbomole (**quantum chemical calculation**)

→ **Partitioning coefficients** COSMOtherm (statistical thermodynamics)

→ $K_{WIOM/G}$, $K_{W/G}$

Arp et al. , *Environ. Sci. Technol.*, 42, 5951-5957, 2008.
Wania et al. *Atmos. Chem. Phys.*, 14, 13189-13204, 2014.
Goss. Chemosphere, 64, 1369-1374, 2006.

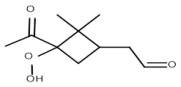
Atmospheric Oxidation Products

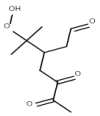
Structures of Atmospheric Oxidation products were generated with the Master Chemical Mechanism (MCM v3.2)

TEXAS A&M UNIVERSITY

- near-explicit chemical mechanism for detailed gas-phase chemical processes
- 143 VOCs, anthropogenic and biogenic species

Reaction products: 3414 non-radical species


C107OOH
MCM1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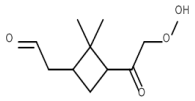
MCM2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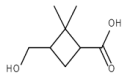
MCM3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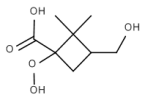
MCM4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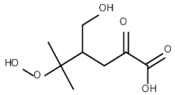
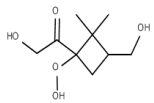
MCM5


C813OOH
MCM6


C89CO2H
MCM7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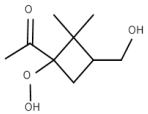
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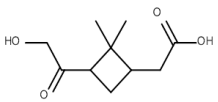
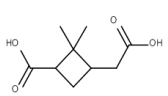
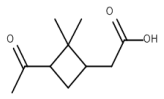
MCM9


HOPINONIC
MCM10

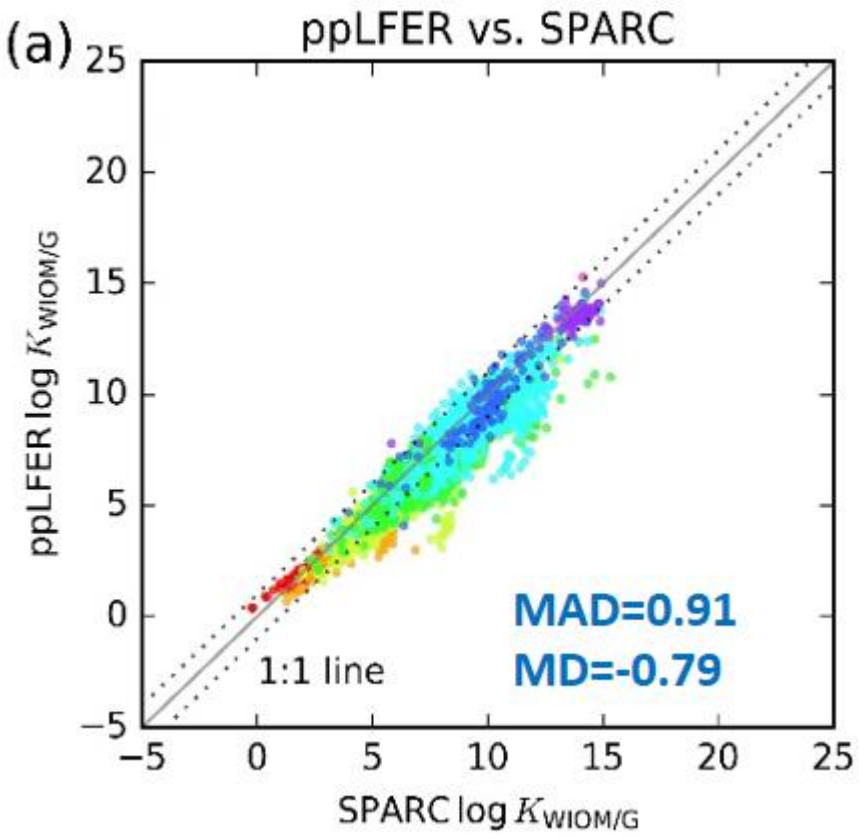

PINIC
MCM11


PINONIC
MCM12

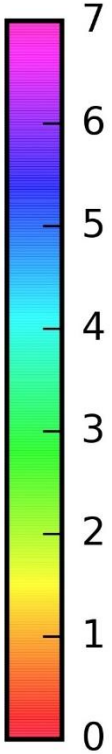
http://mcm.leeds.ac.uk/MCM

Predictions for Atmospheric Oxidation Products

$K_{WIOM/G}$



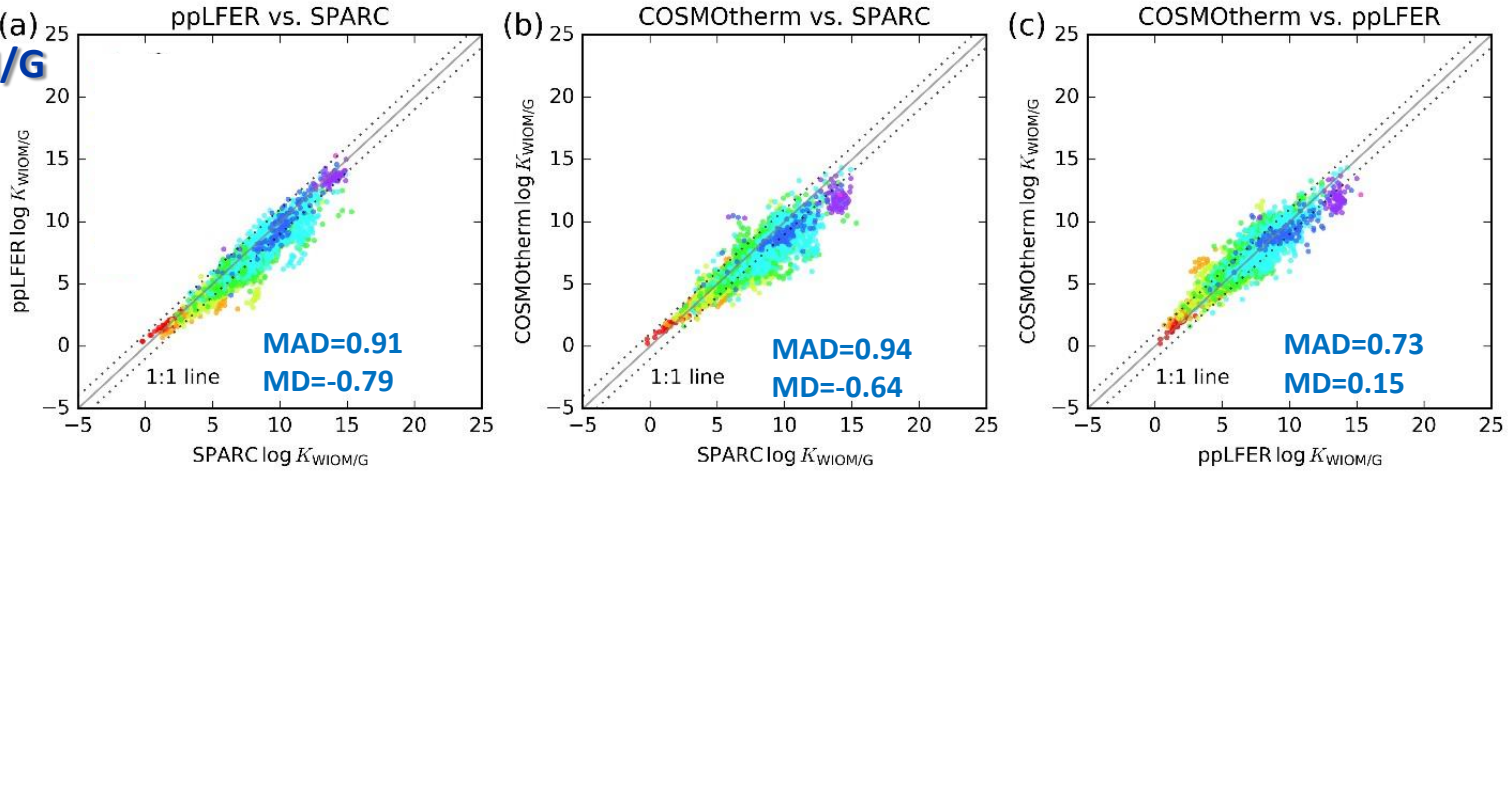
Number of functional groups



MAD: Mean Absolute Difference
MD: Mean Difference

Predictions for Atmospheric Oxidation Products

$K_{WIOM/G}$



- Discrepancy increases with number of functional groups for predicted $K_{W/G.}$

Possible Explanations for the Discrepancies

1. Lack of experimental data for compounds structurally similar to the multifunctional atmospheric compounds for prediction **method calibration**.
→prediction outside the **applicability domain**

- **ppLFER**

$\log K = c + aA + bB + sS + vV + lL$

- **System parameters**: experimental calibration
- **Solute descriptors**: predicted by group contribution method (ABSOLV) based on empirical calibration

- **SPARC**

- Relies to some extent on calibrations with empirical data
- Calibration domain unknown

- **COSMOtherm**

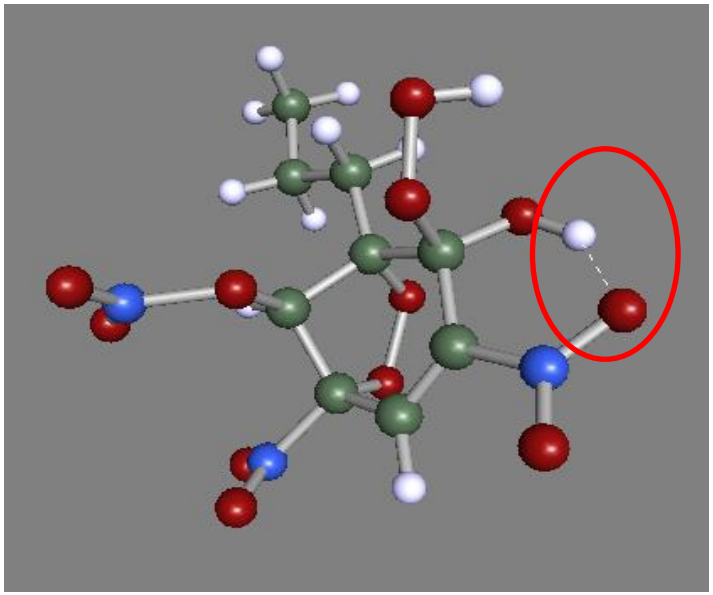
- Relies little on empirical calibrations (not specific for specific compound classes or partition systems)

Platts et al., *J. Chem. Inf. Comput. Sci.,* 39, 835-845, 1999.

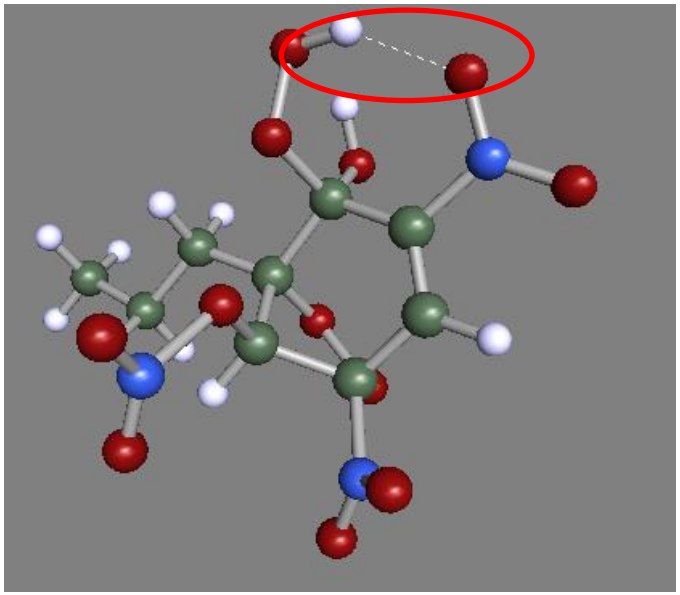
Possible Explanations for the Discrepancies

2. Failure of some prediction methods to account for the various **conformations** that multifunctional compounds can undergo due to **intramolecular interaction** (mostly internal hydrogen bonding)
   →Formation of intramolecular H-bonds competes with the formation of H-bond with water or WIOM.

Example : internal hydrogen bonding for multifunctional compounds



Conformer 1



Conformer 2

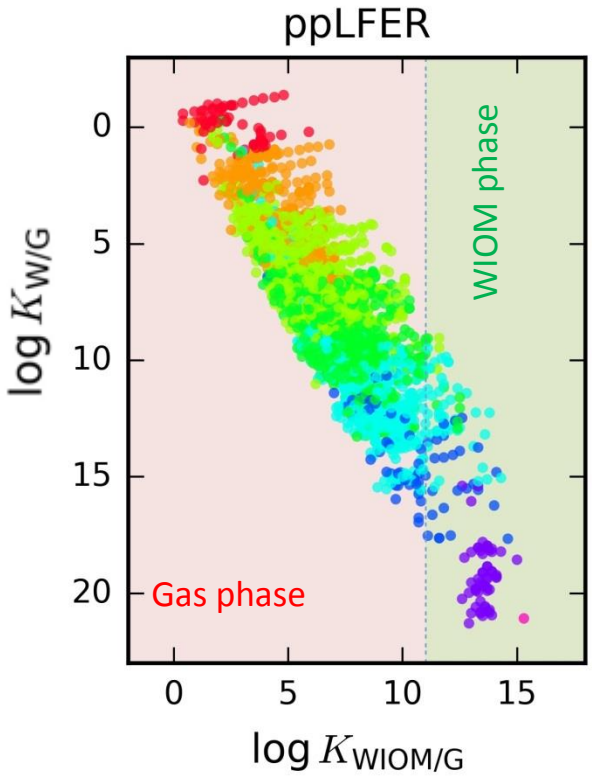
Possible Explanations for the Discrepancies

2. Failure of some prediction methods to account for the various **conformations** that multifunctional compounds can undergo due to **intramolecular interaction** (mostly internal hydrogen bonding)

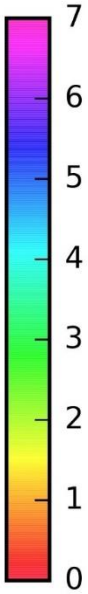
- **ppLFER**
  - Experimentally determined solute descriptors can consider conformation.
  - However, the group contribution based ABSOLV predictions have limited consideration of intramolecular interaction.
- **SPARC**
  - Likely not considering conformation
- **COSMOtherm**
  - Considers conformation and intramolecular interactions
  - Smaller predicted $K_{W/G}$

Predicted Phase Distribution

Organic aerosol:
organic mass: 10 µg m^{-3}



Number of functional groups

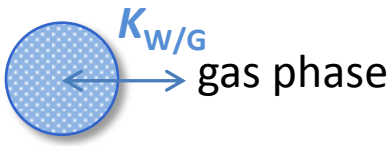


Only 2-5 % of the 3414 compounds have a different preferred phase when a different prediction method is used.

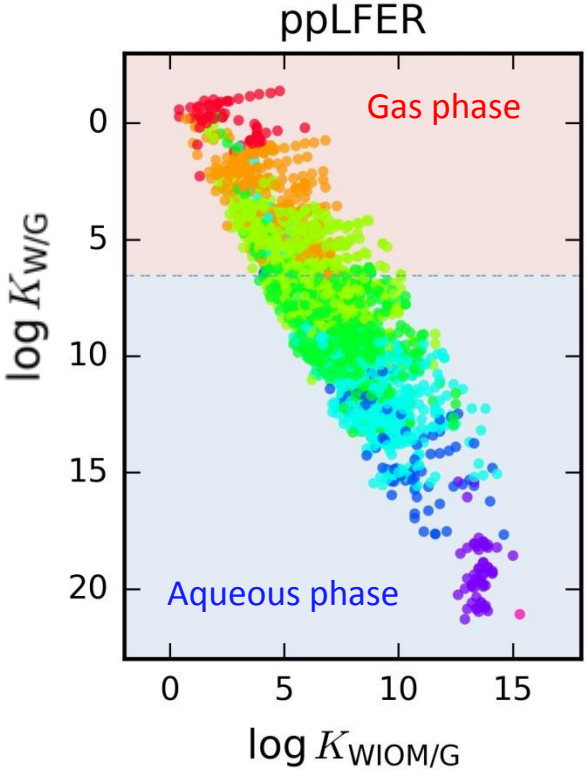
Phase distribution varies only slightly using different prediction method.

Predicted Phase Distribution

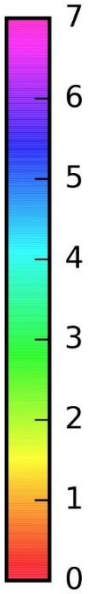
Cloud:
liquid water: 0.3 g m^{-3}



Cloud (W)



Number of functional groups

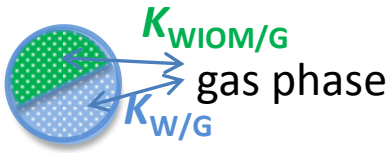


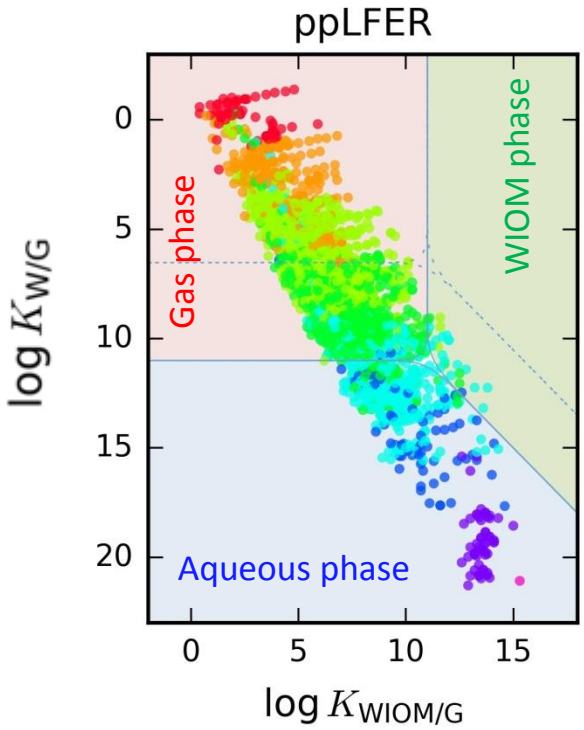
11-34% of the 3414 compounds have a different preferred phase using different prediction method, with COSMOtherm predicting fewer compounds in the cloud.

Phase distribution varies substantially depending on the prediction method.

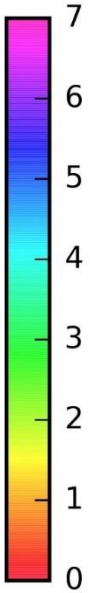
Predicted Phase Distribution

Aerosol with two liquid phases:
liquid water: 10 µg m^{-3}, organic mass: 10 µg m^{-3}





Number of functional groups



- Compounds with ≤2 functional groups: predominantly present in the gas phase.
- Highly functionalized compounds (>3 functional groups): different depending on the method
  - ppLFER and SPARC predict more compounds in aqueous phase than COSMOtherm.

Phase distribution varies substantially, especially for multifunctional compounds.

Conclusions

- How well do partitioning prediction methods perform for atmospheric oxidation products?
  - $K_{WIOM/G}$: generally good agreement using different method
  - $K_{W/G}$: quite large discrepancy, increasing with functional group number

- What determines the uncertainty of the phase partitioning prediction?
  - Reliance on empirical calibration: applicability domain (ppLFER, SPARC)
  - Intramolecular interaction: $K_{WIOM/G}$ vs. $K_{W/G}$, COSMOtherm vs. ppLFER, SPARC

- Does the uncertainty in the prediction affect the estimated phase distribution of atmospheric oxidation products?
  - It depends on atmospheric scenarios and prediction method for $K_{W/G}$.

Scenarios	Different Prediction Method
Organic aerosol (without water)	Similar
Cloud	Different
Aerosol with two liquid phases	Different

Acknowledgements

Natural Sciences and Engineering Research Council of Canada

Conseil de recherches en sciences naturelles et en génie du Canada

Canada

SciNet

University of Toronto
SciNet High Performance Computing Consortium

compute canada | calcul canada

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